

### Claims

The claims defining this invention are as follows:

1. A method of producing a piezoelectric ceramic thick film on a substrate, said method comprising:
  - 5       • providing a piezoelectric ceramic material in powder form;
  - forming a liquid mixture by mixing the powdered material with a liquid phase precursor of a metal oxide of low-melting point, said precursor being adapted to decompose, upon subsequent annealing, into the metal oxide;
  - 10       • drying the liquid mixture to form a precipitate;
  - milling the precipitate to form a powdered precipitate;
  - adding an organic carrier to the powdered precipitate;
  - further milling the precipitate to form a paste;
  - depositing a layer of the paste, as a wet film, onto the substrate;
  - 15       and
  - annealing the layered substrate at a temperature and for a time sufficient to cause transformation of the paste into the thick film.
2. A method according to claim 1, wherein the piezoelectric ceramic material is an inorganic ceramic material which exhibits the piezoelectric effect.
- 20 3. A method according to claim 2, wherein the piezoelectric ceramic material is lead zirconate titanate (PZT).
4. A method according to claim 1, wherein the metal oxide is adapted to form a glass phase upon annealing at elevated temperature.
5. A method according to claim 4, where in the metal oxide is selected from
  - 25       one or more of  $\text{Li}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$ .
6. A method according to claim 5, wherein the liquid phase precursor is a combination of the liquid phase precursors of  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$ .
7. A method according to claim 5 or claim 6, wherein the liquid phase precursor of  $\text{Li}_2\text{O}$  is lithium ethoxide dissolved in ethanol.

8. A method according to claim 5 or claim 6, wherein the liquid phase precursor of  $\text{Bi}_2\text{O}_3$  is bismuth nitrate dissolved in acetic acid.
9. A method according to any one of claims 6 to 8, wherein the liquid phase precursors of  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  are mixed to form a Li-Bi acetic acid solution.
10. A method according to claim 5, wherein the metal oxide is  $\text{PbO}$  and the liquid phase precursor is a solution of lead acetate.
11. A method according to any one of claims 1 to 10, wherein the powdered piezoelectric material is in the form of a suspension in ethanol.
12. A method according to claim 11, wherein the powdered piezoelectric material is fine-grained having an average grain size of below about  $1.0\mu\text{m}$ .
13. A method according to claim 12, wherein the average grain size is about  $0.5\mu\text{m}$ .
14. A method according to any one of claims 1 to 13, wherein the total amount of the metal oxide in the thick film is between about 1% and 5%, by weight.
15. A method according to claim 11, wherein the suspension is mixed with the Li-Bi acetic acid solution, or the lead acetate solution, to form a liquid mixture.
16. A method according to claim 15, wherein the liquid mixture is dried at an elevated temperature to form a dried precipitate.
17. A method according to claim 16, wherein the liquid mixture is dried at a temperature between about  $75^\circ\text{C}$  and  $105^\circ\text{C}$  for up to 10 hours.
18. A method according to claim 16 or claim 17, wherein the dried precipitate is formed into a powdered precipitate.
19. A method according to claim 18, wherein the powdered precipitate is formed by milling the dried precipitate with a ball mill.
20. A method according to claim 18 or claim 19, wherein an organic carrier is added to the powdered precipitate.

21. A method according to claim 20, wherein the organic carrier is selected from one or more of ethyl cellulose, terpineol, and ESL 400 organic binder.
22. A method according to claim 21, wherein the organic carrier is ESL 400 organic binder.
23. A method according to any one of claims 18 to 22, wherein the powdered precipitate and organic carrier are milled to form a paste.
24. A method according to claim 23, wherein the paste is deposited onto a surface of the substrate, by a printing process, as a wet film.
25. A method according to claim 24, wherein the printing process is a screen printing process.
26. A method according to any one of claims 1 to 25, wherein, prior to annealing, the layered substrate is dried.
27. A method according to any one of claims 1 to 25, wherein, prior to annealing, an isostatic pressure is applied to the film.
28. A method according to claim 26, wherein the drying temperature is between about 20°C and about 175°C.
29. A method according to any one of claims 1 to 28 wherein the layered substrate is annealed at a temperature of between about 800°C and about 1000°C.
30. A method according to claim 29, wherein the annealing is conducted for between about 10 minutes and about 4 hours.
31. A method according to any one of claims 1 to 30, wherein the substrate is formed of silicon.
32. A method according to any one of claims 1 to 31, wherein the surface of the substrate has a coating of platinum and the paste is deposited on this platinum coating.
33. A method according to any one of claims 1 to 32, wherein a metal electrode is formed on the piezoelectric ceramic thick film.

- 34. A method according to claim 33, wherein the metal is silver and the electrode material is deposited on the film by a screen printing process.
- 35. A method according to claim 34, wherein the layered substrate is fired at elevated temperature to form the electrode.
- 5 36. A method of producing a piezoelectric ceramic thick film on a substrate, said method being substantially as hereinbefore described with reference to Figure 1 and Example 1 or to Example 2.
- 37. A substrate having a piezoelectric ceramic thick film thereon, formed according to the method of any one of claims 1 to 36.
- 10 38. A piezoelectric sensor or actuator having a piezoelectric ceramic thick film, wherein said thick film has been formed on said substrate according to the method of any one of claims 1 to 36.